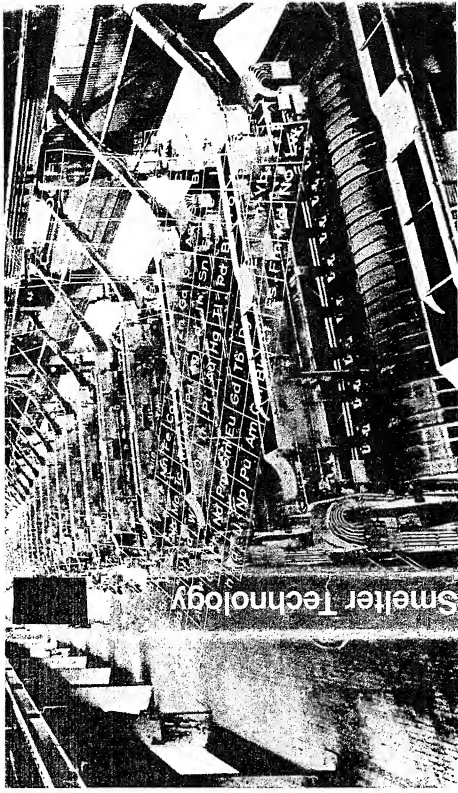


EXHIBIT A



Aluminum Smelter Technology

K. GRJOTHEIM and B. J. WELCH

Aluminium Smelter Technology

A Pure and Applied Approach



ALUMINIUM-VERLAG DÜSSELDORF

AUTHORS' ADDRESSES:

Gjroheim, Kai
Department of Chemistry
University of Oslo
Oslo, Norway

Welch, Barry J.
Department of Industrial Chemistry
School of Chemical Technology
University of New South Wales
Kensington, Australia

CONTENTS

PREFACE	VII
1. ALUMINIUM PRODUCTION	1
Scope	1
1.1 History	1
1.2 Trends in aluminium production	2
1.3 Fundamentals of the present process	4
1.4 Alternative extraction processes	9
1.4.1 Aluminium production by electrolysis of aluminium chloride	9
1.5 Glossary in aluminium smelting	10
2. MATERIAL REQUIREMENTS FOR ALUMINIUM PRODUCTION	14
Scope	14
2.1 Marketable grades of aluminium	14
2.1.1 Pure aluminium	14
2.1.2 Alloys	14
2.2 Sources of alumina	15
2.3 The Bayer process	17
2.3.1 Extraction	18
2.3.2 Decomposition	21
2.3.3 Calcination	21
2.4 Fluorides	22
2.4.1 Cryolite and sodium fluoride	22
2.4.2 Aluminium fluoride	23
2.4.3 Calcium fluoride	24
2.4.4 Magnesium fluoride	24
2.4.5 Lithium fluoride	24
2.5 Carbons	24
	V

ISBN 3-87017-132-4

© Copyright by Aluminium-Verlag GmbH, Düsseldorf, 1980.

Postal address: P.O.B. 1207, Königsallee 36, D-4000 Düsseldorf 1 (FRG).

Telex (02 11) 32 08 21.

All rights reserved, in particular rights of translation into other languages. No part of this publication may be reproduced or transmitted in any form or by any means, electronic, micrographic, mechanical, photocopying, recording or otherwise, without the prior permission of Aluminium-Verlag.

Printed in the Federal Republic of Germany
Boss-Druck und Verlag, Krefeld

As the objective in extraction is to obtain as low a ratio as possible for the maximum extraction yield in a given digester, the conditions are usually adjusted to achieve this readily, i.e. high sodium hydroxide concentrations and high temperatures. These conditions favour more rapid kinetics, and the extraction is achieved more rapidly. Another advantage is the increased solubility of alumina monohydrate, which can also be present in the bauxite deposit.

Table 2.3 Terms used in alumina extraction plants

Caustic concentration - $[Na_2O]$:	
Strong liquor	200 g Na ₂ O per litre (6.5 molar NaOH)
Pregnant liquor	150 g Na ₂ O per litre (4.84 molar NaOH)
Spent liquor	145 g Na ₂ O per litre (4.68 molar NaOH)
Weak liquor	75 g Na ₂ O per litre (2.4 molar NaOH)
Alumina concentration - $[Al_2O_3]$:	
This is the amount of alumina dissolved in the liquor.	
Ratio:	This is the molar ratio of sodium oxide $[Na_2O]$ to alumina $[Al_2O_3]$.
Strong liquor - ratio 3.9	
Pregnant liquor - ratio 1.9	
Spent liquor - ratio 3.9	
Weak liquor - ratio 2.3	
Diluting:	
This is to reduce the caustic concentration - usually with weak liquor.	
Stabilizing:	
This is to increase the ratio by adding spent liquor.	

However, there are several disadvantages in using high temperatures and high caustic soda concentrations. These include the high pressures that result in the digesting vessels, more severe corrosion problems from the alkaline liquor and also a higher solubility of other oxides in the caustic liquor. The latter gives rise to a less pure product. In view of the disadvantages listed, the processing conditions of an industrial digester must be a compromise between the various factors.

For modern plants, the processing conditions are finely tuned to the specific ore deposit. However, typically, temperatures between 200 and 240 °C are used with caustic concentrations up to 25 wt%. These can bring the extraction time down to less than 2 hours in some instances, but can involve pressures exceeding 30 atm. It is desirable to continue the extraction until the

ratio is below 1.9, i.e. forming a pregnant liquor. The lower the ratio, the more alumina it will tend to precipitate in the decomposition stage. On completion of digestion (or the extraction stage) the solution is fed through a slowly agitated settling tank, where the coarse insoluble material (sand) settles out. The liquor is then diluted and stirred in contact with more insoluble material to allow precipitation of an insoluble sodium aluminium silicate. This removes most of the dissolved silica from the caustic solution, although it is undesirable in that it also causes a wastage of caustic soda and reduces the efficiency of the alumina extraction. Following the desilication stage, the slurry is allowed to separate from the red mud in tray thickeners. This process is usually aided by the addition of a coagulating material such as starch. After filtration, the clear liquor is ready for the second stage of the process, the decomposition of the sodium aluminate liquor.

2.3.2. DECOMPOSITION

For reversing the extraction reaction it is desirable for the physical conditions to be as far below the equilibrium curve as possible. This can be achieved by dilution, cooling, or combination of both, (see Fig. 2.2). As precipitated alumina hydrate can tend to be gelatinous, it is essential to add seed crystals for control of the structure of the precipitate. A large excess of crystalline seed hydrate must therefore be added to the solution and, although the decomposition is still an extremely slow process, the rate increases with the area of seed. Decomposition is usually carried out at approximately 50 °C in stirred vessels, and it requires up to 30 hours for the ratio to change from that of a pregnant liquor (1.9) to a spent liquor (3.9). At this stage, kinetically, the decomposition is too slow, even though equilibrium has not been reached, and therefore decomposition is stopped. The alumina trihydrate is then separated from the spent liquor and the seed crystals sized so that a proportion can be recycled as new seed crystals for subsequent decomposition processing. The spent liquor can be reconcentrated and recycled to digestors with make-up sodium hydroxide.

2.3.3. CALCINATION

After washing and classifying the alumina trihydrate crystals into the size fractions, they are fed to a rotary or fluidized bed calcination kiln. Here they are calcined to remove the water of crystallisation and leave the alumina in a structural form suitable for the electrolytic production of aluminium. The calcination takes place in two stages, with most of the water of the crystallisation being evolved in the temperature region 400–600 °C, leaving the more chemically active gamma alumina form. With further heating, the gamma alumina is converted to alpha alumina which is more inert.

Within the electrolytic industry today, varying proportions of alpha and gamma alumina are considered to be desirable, the proportions being de-

Chemistry of Aluminium, Gallium, Indium, and Thallium
Par Anthony John Downs
Publié par Springer, 1993
ISBN 075140103X, 9780751401035 526 pages

Chemistry of Aluminium, Gallium, Indium, and Thallium - Page 84
de Anthony John Downs - 1993 - 526 pages

This first stage of the Bayer process can be expressed by the equation $\text{Al}_2\text{O}_3 \dots$
Decomposition is commonly carried out at around 50°C in slowly stirred ...

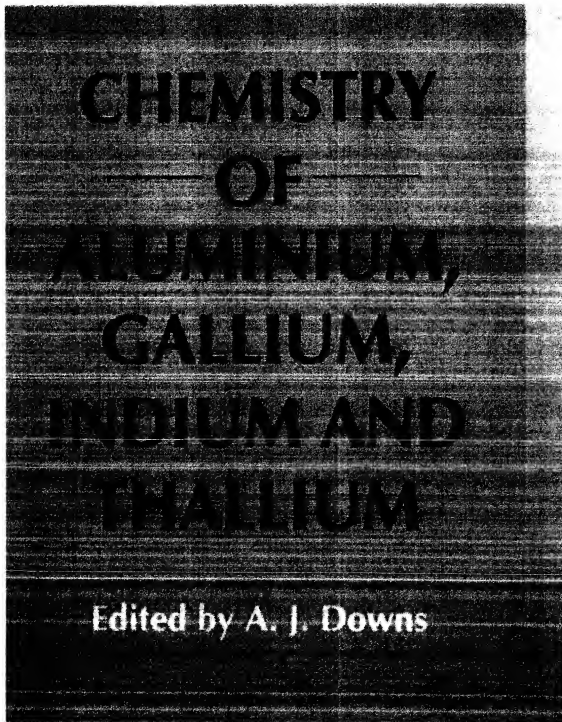


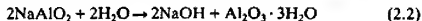
EXHIBIT B

2.2.1 Bayer process for alumina production^{6,7}

The Bayer process was developed and patented by Karl Josef Bayer in Austria in 1888 and essentially involves digesting crushed bauxite in strong sodium hydroxide solutions at temperatures up to 240°C. Most of the alumina is dissolved leaving an insoluble residue known as 'red mud' which mainly comprises iron oxides and silica and is removed by filtration. The particular concentration of sodium hydroxide as well as the temperature and pressure of the operation are optimised according to the nature of the bauxite ore, notably the respective proportions of the different forms of alumina (α , β or γ). This first stage of the Bayer process can be expressed by the equation



Subsequently, in the second stage, conditions are adjusted so that the reaction is reversed. This is referred to as the decomposition stage:



The reaction is achieved by cooling the liquor and seeding with crystals of the trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, to promote precipitation of this compound as fine particles rather than in a gelatinous form. Decomposition is commonly carried out at around 50°C in slowly stirred vessels and may require up to 30 h to complete. The $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is removed and washed and the sodium hydroxide liquor is recycled back to the digestors.

Alumina is then produced by calcining the trihydrate in rotary kilns or, more recently, fluidised beds. Calcination occurs in two stages with most of the water of crystallisation being removed in the temperature range 400–600°C. This produces alumina in the more chemically active γ form which further heating to temperatures as high as 1200°C converts partly or completely to relatively inert α -alumina. Each form has different physical characteristics and individual aluminium smelters may specify differing mixtures of α - and γ -alumina. Currently, Australia produces some 35% of the world's alumina and other major suppliers are Jamaica, Guyana and Brazil.

Invariably alumina produced by the Bayer process has small amounts of impurities such as SiO_2 and Fe_2O_3 but these seldom present problems in subsequent refining. Another impurity is gallium which is present in all bauxites at levels up to 0.01 wt% and is mostly dissolved during digestion. An average large refinery would have a 'throughput' of as much as 500 tonnes of gallium annually. Although the concentration of gallium is very low (e.g. 0.5 g l^{-1}), this is the richest commercial source of gallium, as discussed later.

5. C.M. Lederer and V.S. Shirley, *Table of Isotopes*, 7th edn., Wiley, New York, 1978.

6. K. Gjothelm and B.J. Welch, *Aluminium Smelter Technology*, Aluminium-Verlag, Düsseldorf, 1980.

7. A.R. Burkin, ed., *Production of Aluminium and Alumina*, *Critical Reports in Applied Chemistry*, Vol. 20, Wiley, Chichester, UK, 1987.

8. F.W. Dineson *Can Inst Min Met* 1981 78 153

Light Alloys: From Traditional Alloys to Nanocrystals
Par I. J. Polmear - Publié par Butterworth-Heinemann, 2006
ISBN 0750663715, 9780750663717 421 pages

Light Alloys: From Traditional Alloys to Nanocrystals - Page 16

de I. J. Polmear - 2006 - 421 pages

Immense amounts of **aluminium** are also present in clays, shales and other ...

Decomposition is commonly carried out at around **50 °C** in slowly stirred vessels

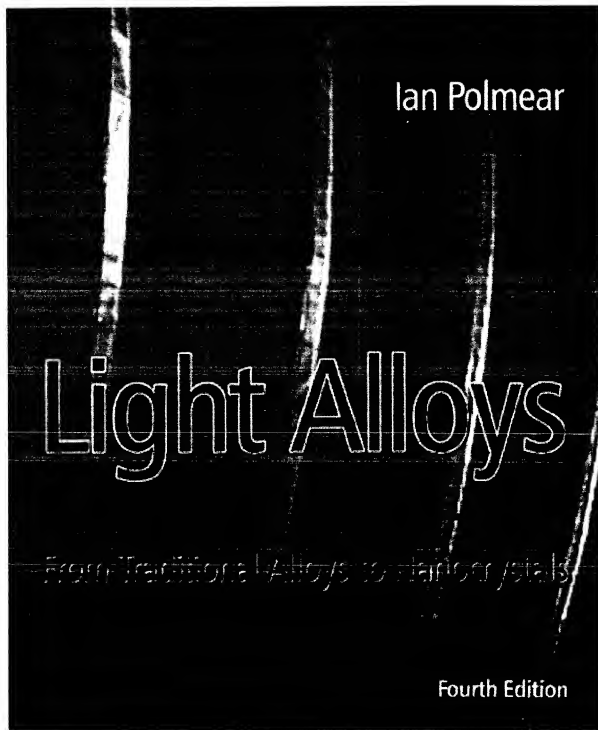


EXHIBIT C

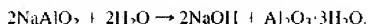
Immense amounts of aluminium are also present in clays, slates and other minerals and the amphoteric nature of aluminium provides the opportunity to use acid as well as alkaline processes for its recovery. As one example, some attention has been given to acid extraction of alumina from kaolinite which is widely distributed as a clay mineral and is a major constituent of the ash in coal. The minerals, nepheline, $\text{Na}_3\text{K}(\text{AlSiO}_4)_4$, and alunite, $\text{KA}_3(\text{SO}_4)_2(\text{OH})_6$, are processed commercially in the Commonwealth of Independent States in plants located in regions remote from sources of bauxite. However, alumina obtained from these and other alternative sources is 1.5–2.5 times more costly than that produced from the Bayer process which is described below.

1.2.1 Bayer process for alumina recovery

The Bayer process was developed and patented by Karl Josef Bayer in Austria in 1888 and essentially involves digesting crushed bauxite in strong sodium hydroxide solutions at temperatures up to 240 °C. Most of the alumina is dissolved leaving an insoluble residue known as 'red mud' which mainly comprises iron oxides and silica and is removed by filtration. The particular concentration of sodium hydroxide as well as the temperature and pressure of the operation are optimized according to the nature of the bauxite ore, notably the respective proportions of the different forms of alumina (α , β , or γ). This first stage of the Bayer process can be expressed by the equation:



Subsequently, in the second stage, conditions are adjusted so that the reaction is reversed. This is referred to as the decomposition stage:



The reverse reaction is achieved by cooling the liquor and seeding with crystals of the trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, to promote precipitation of this compound as fine particles rather than in a gelatinous form. Decomposition is commonly carried out at around 50 °C in slowly stirred vessels and may require up to 30 h to complete. The trihydrate is removed and washed, with the sodium hydroxide liquor being recycled back to the digestors.

Alumina is then produced by calcining the trihydrate in rotary kilns or, more recently, fluidized beds. Calcination occurs in two stages with most of the water of crystallization being removed in the temperature range 400–600 °C. This produces alumina in the more chemically active γ -form which further heating to temperatures as high as 1200 °C converts partly or completely to relatively inert